Precision cutting of nanotubes with a low-energy electron beam

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We report on a method to locally remove material from carbon and boron nitride nanotubes using the low-energy focused electron beam of a scanning electron microscope. Using this method, clean precise cuts can be made into nanotubes, either part-way through (creating hingelike geometries) or fully through (creating size-selected nanotube segments). This cutting mechanism involves foreign molecular species and differs from electron-beam-induced knock-on damage in transmission electron microscopy. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1857081]

Nanotubes (such as those formed from carbon[1] and boron-nitride[2]) are versatile nanoscale building blocks which have already been incorporated into a variety of useful devices. Although nanotubes are relatively easy to synthesize, at present it is difficult to control at the synthesis level the geometrical configurations, including length, number of walls, chirality, etc. Of great utility would be a method whereby the geometrical features of nanotubes could be altered postsynthesis, either before or after their incorporation into functional devices.

A versatile method for cutting nanotubes would be particularly useful. Nanotube devices are often made by poorly controlled solution deposition or chemical growth techniques, which can easily lead to device components contacting multiple nanotubes where only one is desired. A method for removing excess nanotubes is therefore required. Other applications, such as carbon nanotube tipped atomic force microscopy (AFM) cantilevers,[3] require that nanotubes be cut down to a certain length for optimum device performance. Finally, certain nanotube-based systems, such as nanoscale rotational bearings, require nanotubes that have been selectively damaged.[4,5]

Several methods for cutting or damaging nanotubes have been previously reported, each with distinct disadvantages. Chemical etches have been used to shorten nanotubes,[6] but these etches indiscriminately damage all high curvature regions of a nanotube and are difficult to control. Highly selective damage has been induced in transmission electron microscopes (TEM), using both voltage pulses applied through a nanomanipulator[7] and knock-on damage caused by the high-energy electron beam.[8] TEM work, however, requires an electron-transparent substrate, which severely limits the types of devices that can be imaged. Similarly, while nanotubes can be cut by voltage pulses applied through a scanning tunneling microscope (STM) tip[9] or AFM tip,[10] many nanotube-containing devices are either too delicate or too irregular to be imaged by STM or AFM, or lack a conductive substrate (which is necessary for STM). Scanning probe methods are also very time consuming. Finally, passing current through an electrically contacted nanotube may cut it,[11] but the exact location of the cut is uncontrollable and the current may also damage the primary nanotube used in the device.

We present here a technique by which nanotubes are controllably damaged using the low-energy focused electron beam of a scanning electron microscope (SEM). We are able to cut through nanotubes, or, with smaller doses, to create hingelike defects. Examination of damaged nanotubes in a TEM reveals that material is removed with minimal damage to surrounding areas. Our method is compatible with most device architectures (the nanotube need only be viewable in a SEM), offers complete control over where the nanotube will be cut, and is relatively fast, requiring only several minutes to load, locate, and cut the nanotube in the SEM.

Multiwall carbon nanotubes synthesized by the standard arc-discharge technique were dispersed in either orthodichlorobenzene or isopropyl alcohol (no dependence upon the particular solvent used was seen). The nanotube solution was then deposited either onto TEM grids coated with lacey carbon for TEM imaging or onto a silicon oxide surface for *in situ* electrical transport studies. Electrical contacts were patterned by standard electron-beam lithography and were composed of gold over a thin chromium adhesion layer. The samples were then loaded for cutting into an FEI XL30 Sirion SEM. During cutting, the SEM was operated in line scan mode at maximum magnification ($10^6\times$), with the nanotube axis perpendicular to the scan line. Several different gases were introduced through a leak valve, and partial gas pressures were measured with a Stanford Research Systems SRS200 residual gas analyzer. Absolute pressure was measured using a Bayard–Alpert ion gauge and a Terranova 934 controller programmed with the appropriate gas constants. A Keithley 2400 source meter was used for transport measurements. TEM images were taken before and after cutting in a JEOL 2010 TEM using an acceleration voltage of 100 keV.

We were able to cut through nanotubes at a variety of acceleration voltages, beam currents, and gas pressures within the microscope chamber. The cuts were seen as a gradual decrease in height and width of the nanotube line scan profile, and the decrease accelerated as the cut neared completion. We could interrupt any cut by blanking the beam or switching the microscope out of line scan mode. If the nanotube was suspended, as on a TEM grid, a sufficiently damaged region would often act as a loose hinge, with the nanotube swinging under the charging influence of the electron beam. We have also been able to make oblique cuts by rotating the scan line relative to the nanotube, which may be useful for making sharpened AFM tips.

Figure 1 shows a nanotube on a TEM grid before and after cutting. Figure 1(a) shows the uncut nanotube suspended across a gap. The turbulent deposition method dis-

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placed the ends of the nanotube perpendicular to its longitudinal axis, subjecting it to a shear strain which was maintained by contact with the grid and other deposited material. This shear strain was released when the nanotube was cut, and the two sections of the nanotube straightened out, as seen in Fig. 1(b). Figure 1(c) is a close-up image of a section of the pristine nanotube before cutting. Figure 1(d) shows the same section after cutting, with the two cut sections rotated and aligned to vertically correspond with Fig. 1(c). A comparison of these last two images shows that the cut removed approximately 40 nm of material. This gap is larger than the ~3 nm beam spot size, most probably due to beam position drifts over the duration of the cutting process. Nonetheless, the damage induced by the electron beam was confined to the immediate region of the cut, with equal damage done to each subsequent layer of the multiwall nanotube.

The most important factor affecting the cutting speed was the presence of water vapor within the chamber. Figure 2 shows the results of cutting through a single nanotube at several points along its length in different atmospheres, with an acceleration voltage of 1 keV and a beam current of 118 pA. At total pressures below 2×10^{-6} Torr, where most of the residual pressure was due to water vapor, nanotubes could be exposed to the beam for over 10 min and still not be visibly damaged. Bleeding in nitrogen to a pressure of 7.5×10^{-5} Torr did not significantly affect the cutting time. Bleeding in hydrogen at the same pressure resulted in slightly faster cuts, but this may be due to a higher partial pressure of water (our hydrogen source contained a partial pressure of water over 50% higher than in the other gasses). Oxygen consistently increased cutting speed up to twice as fast. Water, at the same pressure, would increase the cutting speed even more, up to ten times as fast.

Electron-beam-induced mass loss is a well known effect in electron microscopy of biological samples.[12] Studies have found that a common source of mass loss is caused by the presence of water.[13,14] Radiolysis of water molecules is the driving force behind this etching mechanism:[15] Highly reactive $OH\cdot$, $H\cdot$, and $HO_2\cdot$ radicals can react with carbon atoms to form CO, CO_2, various hydrocarbons and hydrogen gas, leading to mass loss of the original carbonaceous specimen (and similar reactions can be expected when oxygen molecules are ionized in the vicinity of the sample). We propose that this etching mechanism is responsible for damaging the nanotubes. This mechanism is fundamentally different from previously reported electron-beam-irradiation damage of nanotubes as seen in a TEM, where incident electrons eject carbon atoms from the nanotube and must have an incident energy of at least 86 keV.[16]

Interestingly, we found that bundles of nanotubes would consistently be cut faster than individual nanotubes, despite the greater amount of material that must be removed. Theoretical calculations of water adsorption on the outside of nanotube bundles have shown, however, that water molecules will be adsorbed first into the groove between two nanotubes and only at higher densities will they then be adsorbed onto the entire nanotube surface.[17] This suggests that bundles will adsorb more water at a given pressure than individual nanotubes. Since the presence of water greatly accelerates cutting, we can therefore expect nanotube bundles to be easier to cut.

Two-contact electrical transport shows a steady increase in the resistance of the nanotube during the cut, with no steps or jumps showing opening or closing of discrete conductance channels. We did find, however, that by passing current through the nanotube during a cut we could reduce the damage done to the nanotube and greatly increase its lifetime under the beam. For example, putting 1.7 V across a nanotube with an initial resistance of 15 kohms would decrease the cutting rate by a factor of 4 (this cut took 20 min, while two separate cuts on the same nanotube with no voltage applied took 5 min each).

Resistively heating the nanotube may reduce the damage through two possible mechanisms. It has been shown that raising the temperature of nanotubes to over 300 °C reduces knock-on damage by annealing out defects via the increased mobility of interstitial atoms.[18] Also, by increasing the temperature of the nanotube, we decrease the sticking coefficient

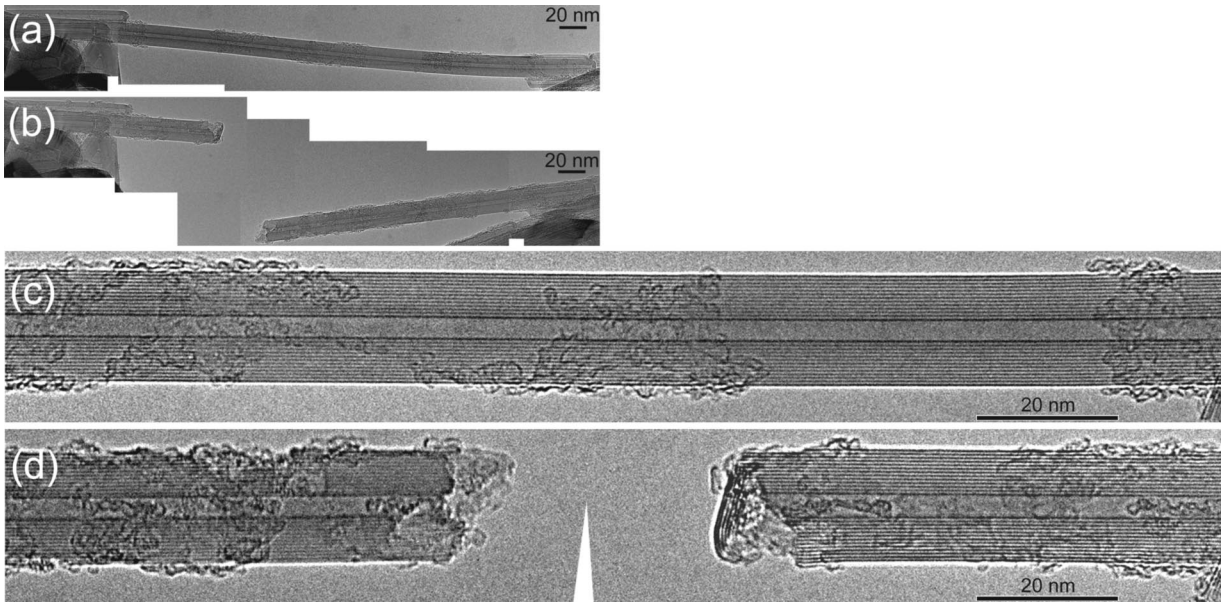

FIG. 1. Composite TEM micrographs of **(a)** a nanotube in its pristine state suspended on a TEM grid, **(b)** the same nanotube after cutting, **(c)** a close-up image of the same nanotube, and **(d)** the cut segments of the nanotube, rotated and aligned to vertically correspond with the same sections in **(c)**. The scale bars are 20 nm.

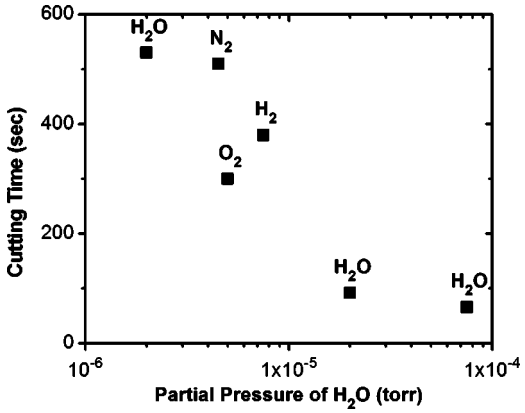

FIG. 2. Cutting times for multiple cuts on a single nanotube in different atmospheres. The partial pressure of water is shown on the horizontal axis, while the majority gas is shown above the data points. The total pressure was 7.5×10^{-5} Torr during the N_2, O_2, and H_2 trials.

of water molecules impinging on the surface, thus limiting the number of molecules present to aid in the cut.

Figure 3 shows the results of cutting two nanotubes exposed to different partial pressures of water at various beam currents. At a higher partial pressure, increasing the beam current speeds up the cutting process. This is simply the consequence of adding more energy to the system, thus increasing the rate of the chemical reaction. At low water vapor pressure (2×10^{-6} Torr), however, this effect was greatly suppressed, and even high beam currents ($\sim$500 pA) would not significantly increase cutting speed. Therefore, we propose that at low pressures, the rate is limited by the amount of water present rather than the amount of energy supplied by the electron beam.

Figure 4(a) shows cutting times for multiple cuts on several nanotubes at different acceleration voltages. Contrary to naïve expectation, increasing the acceleration voltage of the electron beam increases the cutting time. This effect is due to the cross section for the ionization of a water molecule decreasing as the incoming electrons become more energetic. Schutten *et al.*[19] have measured the total ionization cross section for water for this range of electron energies. A normalized plot made by rescaling the cutting times of different nanotubes to match at common acceleration voltages is shown in Fig. 4(b), together with a plot of the inverse of the total ionization cross section.

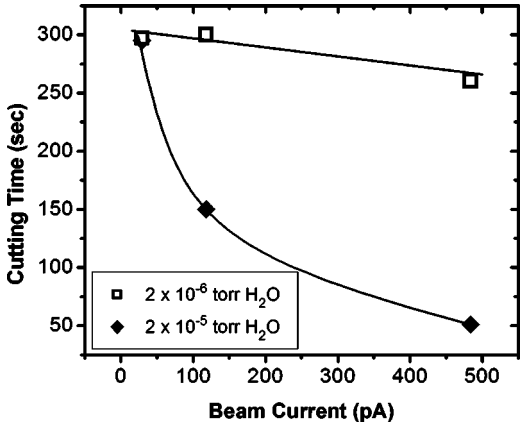

FIG. 3. Cutting times for multiple cuts on two nanotubes in different atmospheres at different beam currents. In both cases, the majority gas was water vapor. The dashed lines are guides for the eye.

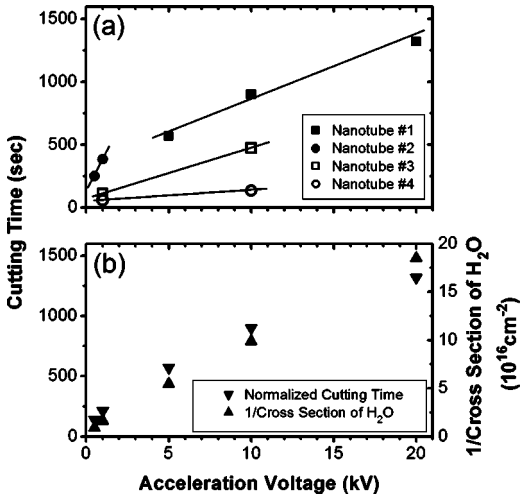

FIG. 4. Cutting time vs acceleration voltage. **(a)** Cutting times for multiple cuts on several nanotubes at different electron beam energies. The dashed lines are guides for the eye. **(b)** Normalized cutting data from three nanotubes at different electron-beam energies. The inverse of the total ionization cross section for water molecules as a function of electron energy is also plotted, and follows the same trend.

We were careful to minimize the beam exposure while locating and imaging the nanotubes prior to cutting. From our results, it is evident that precautions must be taken during all SEM/nanotube experiments to limit beam-induced damage. We have also been able to damage and cut inorganic nanostructures (boron-nitride nanotubes), extending this caveat to SEM work on all sensitive nanomaterials.

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